

**\* NOTICES \***

**JPO and INPIT are not responsible for any damages caused by the use of this translation.**

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : **10-004212**

(43)Date of publication of application : **06.01.1998**

(51)Int.Cl. **H01L 33/00**

**H01L 29/06**

(21)Application number : **08-155566** (71)Applicant : **JGC CORP**

(22)Date of filing : **17.06.1996** (72)Inventor : **AMAMIYA  
YOSHINORI  
WATANABE  
TAKESHI  
MIYAZAKI  
HIROSHI**

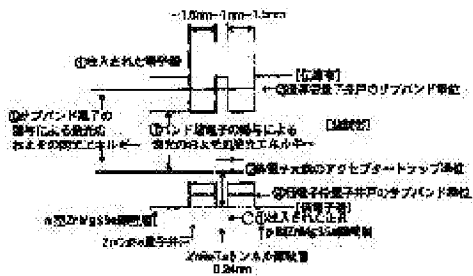
**(54) LIGHT-EMITTING DIODE**

(57)Abstract:

**PROBLEM TO BE SOLVED:** To improve high brightness and reliability by giving the luminous characteristics of shortwave length to a light emitting diode by a method wherein a barrier inserting layer, in which an equielectron constituent element is added, is provided in an i-type quantum well layer, and the barrier inserting layer is formed in the thickness with which tunneling of electron and hole occurs.

**SOLUTION:** This light-emitting diode is constructed in a double heterostructure in which an i-type quantum well layer is pinched between a p-type semiconductor layer and an n-type semiconductor layer,

and a barrier inserting layer, where an equielectron element, having the electron equal to the above-mentioned constituent element is added, is provided in the i-type quantum well layer. For example, i-type quantum well layer, in which an intrinsic (i-type) ZnCdSe layer 23 is used as a well layer using an n-type ZnMgSSe layer 21 as a barrier layer, and a p-type ZnMgSSe layer 22, is used as an active layer, and a Te-added



ZnSe barrier inserting layer 24 is formed on the center part of the quantum well layer. Besides, the barrier inserting layer is formed in the thickness with which a tunneling is generated, i.e., 2nm or smaller, for example, and the film thickness of the i-type quantum well layer is less than 4nm.

## CLAIMS

---

[Claim(s)]

[Claim 1] In a light emitting diode of double hetero structure which sandwiched i type quantum well layer between a p type semiconductor layer and a n type semiconductor layer, A quantum well type light emitting diode being a grade which possesses a barrier insertion layer which added an isoelectronic element of this composing element, and from which thickness of said barrier insertion layer produces tunneling of an electron and an electron hole in said i type quantum well layer.

[Claim 2] The light emitting diode according to claim 1, wherein thickness of said barrier insertion layer is 2 nm or less.

[Claim 3] The light emitting diode according to claim 1, wherein thickness of said i type quantum well layer is 5 nm or less.

[Claim 4] Said p type semiconductor layer and a n type semiconductor layer are  $\text{Zn}_{1-x-y-z}\text{Mg}_x\text{Cd}_y\text{Mn}_z\text{S}_{1-l-m}\text{Se}_l\text{Te}_m$ , and said quantum well layer, It comprises an i type quantum well layer which makes  $\text{Zn}_{1-x-y-z}\text{Mg}_x\text{Cd}_y\text{Mn}_z\text{S}_{1-l-m}\text{Se}_l\text{Te}_m$  a well layer, And the light emitting diode possessing a  $\text{ZnMgCdMnSSe}$  barrier insertion layer which contains isoelectronic elements, such as Te, in this quantum well according to claim 1.

[Claim 5] Said quantum well layer in i type quantum well layer which consists of  $\text{Zn}_{1-x-y-z}\text{Mg}_x\text{Cd}_y\text{Mn}_z\text{S}_{1-l-m}\text{Se}_l\text{Te}_m$ , What inserts a  $\text{ZnMgCdMnSSe}$  barrier insertion layer containing isoelectronic elements, such as Te, via  $\text{Zn}_{1-x-y-z}\text{Mg}_x\text{Cd}_y\text{Mn}_z\text{S}_{1-l-m}\text{Se}_l\text{Te}_m$  barrier layer, The light emitting diode according to claim 1 which forms repeatedly a term two or more rounds, and is characterized by things.

---

## DETAILED DESCRIPTION

---

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the light emitting diode of a blue field from a light emitting diode and the green especially used as a display, and a pilot lamp or a light source.

[0002]

[Description of the Prior Art] Although the high-intensity blue light-emitting diode using III-V fellows' gallium nitride indium (GaInN) is produced, in mass production nature, a price side, etc., it is not enough.

[0003] It is cheap as a substrate for [ one ] epitaxial growth of the reason, and is being unable to use a conductive high semiconductor substrate. Since a conductive substrate cannot be used, element structure becomes complicated on account of electrode extraction.

[0004] On the other hand by II-VI group, high-intensity blue light is obtained with the ZnCdSSe system quantum well type light emitting diode, Although high-intensity green emission is obtained with the double hetero type light emitting diode or the quantum well type light emitting diode of ZnMgSSe/ZnCdSe which makes ZnSeTe a luminous layer, also in any, there is a problem in a life etc.

[0005] For example, there is a double hetero type light emitting diode which makes ZnSeTe a luminous layer as shown in drawing 10 (crystal growth by Eason and others: D.Eason et al, J.Crystal Growth, 150 (1995) 718-724). In this light emitting diode, the ZnSeTe active layer 13 of i (genuineness) mold is formed in the ZnSe substrate 11 surface via the n type ZnSe contact layer 12, Furthermore, the ZnSeTe contact layer 15 and the HgSe contact layer 16 are formed in this upper layer via the p type ZnSe barrier layer 14, and the metal electrodes 17 and 18 are formed, respectively on this HgSe contact layer 16 and the n type ZnSe barrier layer 12.

[0006] The active layer has here the structure where the  $\text{ZnSe}_{0.9}\text{Te}_{0.1}$  active layer 13 is formed on the n type ZnSe barrier layer 12, and the p type ZnSe barrier layer 14 is further formed in this upper layer, as the extension mimetic diagram near the active layer is shown in drawing 11. In the n type ZnSe barrier layer 12, 3000 nm and the  $\text{ZnSe}_{0.9}\text{Te}_{0.1}$  active layer 13 are set to 50-100 nm, and, as for such thickness, the p type ZnSe barrier layer 14 has become about 1000 nm, respectively.

[0007] Although this light emitting diode is efficient high-intensity, as shown in drawing 12, as for a current injection (EL) spectrum, a

broadcloth single peak is shown.

[0008]A photoluminescence (PL) spectrum when the composition ratio of Se and Te of ZnSeTe is changed is shown in drawing 13. Generally, in the range which can form an excitation state, PL spectrum of a luminous layer shows spectral shape similar to EL spectrum.

[0009]First, as shown in drawing 13, by PL spectrum of  $\text{ZnSe}_{1-x}\text{Te}_x$ , x follows on increasing and a peak shifts in the direction of S2 which is a low energy side from S1 which is a high energy side. x= 0.01 and c of a are x= 0.02 x= 0.003 and b here. It is known that x will follow on increasing also at the same temperature from another experiment, and S2 will become dominant. Surely with the element of the conventional example mentioned above, EL spectrum of drawing 12 corresponds to S2 by the reason that it is x= 0.1, and it is a field where S2 is observed since it operates at a room temperature.

[0010]

[Problem(s) to be Solved by the Invention]The spectrum acquired by performing current injection for the element of this conventional example in a room temperature shows the appearance top and single peak which have a peak in 512 nm and pull the skirt to the long wavelength side, as shown in drawing 12.

[0011]However, in order to obtain desirable blue light, it is necessary to eliminate the skirt by the side of long wavelength, and to achieve the short wavelength formation of a luminous wavelength in a broadcloth peak.

[0012]This invention was made in view of said actual condition, and has the luminescent characteristic of short wavelength, and an object of this invention is to provide a reliable light emitting diode with high-intensity.

[0013]

[Means for Solving the Problem]So, in this invention, it is characterized by being a grade which possesses a barrier insertion layer which adds an isoelectronic element and from which thickness of this barrier insertion layer produces tunneling of an electron and an electron hole in a quantum well in a light emitting diode which makes a quantum well layer an active layer.

[0014]Namely, in a light emitting diode of double hetero structure which sandwiched i type quantum well layer between a p type semiconductor layer and a n type semiconductor layer in this invention, A barrier insertion layer which added an isoelectronic element which has an electron equal to this composing element in said i type quantum well layer is provided, and it is characterized by being a grade from which thickness of said barrier insertion layer produces tunneling. Thickness of said barrier insertion layer is characterized by being 2 nm or less.

[0015]Thickness of said i type quantum well layer is characterized by

being 4 nm or less.

[0016] Said p type semiconductor layer and a n type semiconductor layer, Are  $\text{Zn}_{1-x-y-z}\text{Mg}_x\text{Cd}_y\text{Mn}_z\text{S}_{1-l-m}\text{Se}_l\text{Te}_m$  and said quantum well layer, It comprises an i type quantum well layer which makes  $\text{Zn}_{1-x-y-z}\text{Mg}_x\text{Cd}_y\text{Mn}_z\text{S}_{1-l-m}\text{Se}_l\text{Te}_m$  a well layer, And a ZnMgCdMnSse barrier insertion layer which contains isoelectronic elements, such as Te, in this quantum well was provided. In i type quantum well layer as for which said quantum well layer consists of  $\text{Zn}_{1-x-y-z}\text{Mg}_x\text{Cd}_y\text{Mn}_z\text{S}_{1-l-m}\text{Se}_l\text{Te}_m$  desirably, What inserts a ZnMgCdMnSse barrier insertion layer containing isoelectronic elements, such as Te, is repeatedly formed via  $\text{Zn}_{1-x-y-z}\text{Mg}_x\text{Cd}_y\text{Mn}_z\text{S}_{1-l-m}\text{Se}_l\text{Te}_m$  barrier layer a term two or more rounds.

[0017]

[Function] For example, as a band structure figure is shown in drawing 1, in the n type ZnMgSse layer 21 and the p type ZnMgSse layer 22 as a barrier layer. In the light emitting diode in which the ZnSe barrier insertion layer 24 which made the active layer i type quantum well layer which makes a well layer the intrinsic (i type) ZnCdSe layer 23, and added Te to the center portion of this quantum well was formed. The poured-in electron hole goes into a valence-band subband first, the electron poured in on the other hand goes into a conducting-zone subband, and, subsequently it is thought that the electron of a subband and the electron hole of a subband form a quantum well free exciton. An electron hole and an electron form the restraint exciton bound to Te which is an isoelectronic element. Under the present circumstances, the energy of a restraint exciton falls from the energy of a quantum well free exciton by stabilizing with an isoelectronic element. The bound energy of a restraint exciton shows broadcloth energy distribution. Usually, in EL luminescence, luminescence from S2 state rules over. A part of this restraint exciton is considered that the electron which exists near the band end is participating in formation.

[0018] The quantum well free exciton formed in a quantum well is eased by luminescence and nonluminescent recombination via the level which recombines as it is, and eases or is formed into a forbidden band of the crystal defect of a rearrangement, an impurity, etc. The recombination of the bound exciton with which the isoelectronic trap was supplemented is radiative recombination, and since the recombination rate is large, it is thought by going via an isoelectronic trap that luminescence probability is raised. The bound energy of an isoelectronic trap has broadcloth distribution, and it accepts as two peaks, such as S1 and S2, in 400 to 600 nm. The reason S1 and S2 appear is set to S2 when a band and an exciton are bound to two or more isoelectronic elements, and it is thought that it is because S1 is given in the case of one. It differs by how

many isoelectronic elements are distributed over the orbital (almost Bohr radius) range of a bound exciton by what kind of arrangement also in two or more case.

[0019]When using a quantum well for an active layer raises luminous efficiency, the effective thing is known from the former, but in this invention, by inserting a barrier insertion layer in this quantum well further, it discovers that luminous efficiency can be raised further and made paying attention to this. That is, if a barrier insertion layer is inserted in the central part there where electron and electron hole's existence probability is large in a quantum well, although a wave function changes compared with insertion before, it is more advantageous than inserting in the central part at the point that electron and electron hole's existence probability is large inserts in an end. By inserting a barrier layer in a quantum well layer, when subband level can be raised and luminescence of a short wavelength region is obtained, it is advantageous. Since the breadth of the orbit of an isoelectronic trap bound exciton is considered to be about 1.5 nm in radius, about 1.5 nm is suitable for the quantum well width which sandwiches \*\*\*\*\* respectively, and it can acquire sufficiently big subband energy in this case. quantum well layer overall width shall be 5 nm or less -- \*\*\*\* -- better -- \*\*. That is, the subband electron of the conductor side quantum well is considered to become easy to form the isoelectronic trap restraint exciton which involves by narrowing quantum well overall width.

[0020]There is a suitable energy state in the electron from a quantum well free exciton to an isoelectronic trap bound exciton, and shift of an electron hole, and even if it compares and is smaller than a barrier insertion layer, A barrier insertion layer can be penetrated and to enable transition to an isoelectronic bound exciton is considered by the tunnel effect. Incidentally, the thickness of this barrier insertion layer should just be a grade which may produce the tunnel effect, and it is desirable to be referred to as 2 nm or less. By making into an about 0.5-nm thin layer the ZnSeTe layer containing an isoelectronic trap, two or more vertical Te's to this layer existence probability is stopped, and the distribution which appears as the skirt in the low energy side of S2 can be controlled. As for the band offset of a tunnel barrier layer, it is desirable that it is comparable as them of the barrier layer which sandwiches the whole quantum well. In this case, injected charges can go into each quantum well, without almost being influenced by a tunnel barrier layer in the range of that mean free path.

[0021]

[Example]Hereafter, this invention is explained in detail, referring to drawings. As shown in drawing 2, this light emitting diode, Gallium arsenide. (GaAs) The n type ZnSSe cladding layer 3 of 1000 nm of



thickness laminated one by one on the substrate 2, the ZnCdSe layer 4 of 3 nm of thickness, and the ZnSe barrier insertion layer 5 of Te dope of 1 nm of thickness inserted in the center of this ZnCdSe layer 4 the ZnSSe barrier layer 6i which is 10 nm. It inserts, and comprises an active layer you are made to come to form five cycles, and the p type ZnSSe cladding layer 6 of 1000 nm of thickness and the p type inclination potential layer 7 which were further formed in this upper layer, and the n lateral electrode 1 which consists of indium (In) further, and the p lateral electrode 8 which consists of gold are formed.

[0022]The mimetic diagram of the band diagram of this light emitting diode is shown in drawing 3, and EL spectrum is shown in drawing 4.

[0023]As shown in this figure, by a ten atom % grade as a VI group isoelectronic element in the center of the active layer which consists of quantum well layers according to and that Te doped layer with the thickness about a monomolecular layer is inserted, cross protection, etc. Many peaks dissociate, and it appears and it is thought that the intensity ratio of each spectrum changes with the composition of a presentation, thickness, etc. Originally luminescence from an isoelectronic trap is constituted by many peaks. This originates in a trap level changing depending on the bias of distribution of an isoelectronic element. That is, like the place in which many Te elements gathered more, a trap level becomes low and a luminous wavelength long-wavelength-izes it. In this invention, three-dimensional distribution is changed into two-dimensional distribution by making a ZnSe barrier insertion layer thin.

Therefore, it becomes possible to control deep-trap level, and the distribution by the side of low energy is controlled in distribution of S2. When these carry out short wavelength formation of the luminous wavelength, they are effective.

[0024]By setting a luminous layer on the central part of a quantum well layer with high electron and electron hole's existence probability, by raising effectual current injection density, a nonluminescent process can be suppressed and luminous efficiency can be raised.

[0025]Next, this light emitting diode is explained in detail according to a manufacturing process.

[0026]The ZnSSe cladding layer 3 of 1000 nm of thickness and the ZnCdSe layer 4 of 1.5 nm of thickness are formed in the n type GaAs substrate 2 surface with a molecular beam epitaxy (MBE) first (100). Then, the ZnSe barrier insertion layer 5 of Te dope of about 1 nm of thickness is formed in the surface of this ZnCdSe layer 4. Furthermore, the ZnCdSe layer 4 is again formed in this upper layer by an MBE technique. And like the process of pinching the i type ZnSSe layer 6i, and forming the ZnCdSe layer 4 again, the process of forming the ZnSe

barrier insertion layer 5 of Te dope in this surface, and the process of forming the ZnCdSe layer 4 further, The p type ZnSSe cladding layer 6 and the p type inclination potential layer 7 are formed in 3 cycle repetition and also this upper layer for the quantum well structure containing a barrier insertion layer one by one. And it patterns by the usual photolithography, and while forming the n lateral electrode 1 which is from indium (In) on a substrate side finally, the p lateral electrode 8 which consists of gold is formed in the surface side.

[0027]Thus, as a manufacturing process, it is only adding a doping process, and can form very easily.

[0028]Although the ZnSe layer which added Te as an isoelectronic element was used in said example, As shown, for example in drawing 5, without being limited to this as an active layer, Into [ which is not accepted  $\text{Zn}_{0.9}\text{Cd}_{0.1}$  Se-layer 24 ] 49 nm of thickness, 1 nm of ZnSe layers 25 of a tellurium dope may be formed, and this may be repeatedly formed on both sides of the  $\text{ZnSe}_{0.88}\text{Te}_{0.12}$  barrier layer 26 a multi-circumference term.

[0029]The curve a shows the photoluminescence spectra using this active layer to drawing 6. It turns out that the peak is formed in the short wavelength side so that clearly from this figure.

[0030]As shown in drawing 7 as other examples, as an active layer in [ which is not accepted  $\text{Zn}_{0.9}\text{Cd}_{0.1}$  Se-layer 24 ] 33 nm of thickness, ZnSe layer 25 of Te dope of 5 nm of thickness may be formed, and this may be repeatedly formed on both sides of the  $\text{ZnSe}_{0.88}\text{Te}_{0.12}$  barrier layer 26 a multi-circumference term.

[0031]The curve b shows the photograph spectrum using this active layer to drawing 6. It turns out that the peak is formed in the short wavelength side so that clearly from this figure.

[0032]In the structure where a barrier insertion layer is not put in for comparison as shown in drawing 8, it has two peaks, as shown in drawing 9, and it has structure which pulls the skirt to the long wavelength side.

[0033]Although it is easy to produce transition in a thick quantum well with a lattice strain, also in an example, the grating constant between a cladding layer and a well layer has a difference, Although it is easy to produce transition in a thick quantum well, by quantum well overall width being 5 nm or less, energy distortion can be controlled compared with a wide well, and element deterioration can be controlled.

[0034]Thus, it becomes possible also from comparison of drawing 6 and drawing 9 to obtain the luminous layer which has a high peak in the short wavelength side by forming a barrier insertion layer into a quantum well layer like this invention.

[0035]

[Effect of the Invention]As explained above, in this invention, the thin barrier insertion layer which doped the isoelectronic element is formed in the central part of a quantum well layer.

Therefore, it becomes possible to form a semiconductor device with high luminous efficiency.

---

## DESCRIPTION OF DRAWINGS

---

[Brief Description of the Drawings]

[Drawing 1]The figure showing the band diagram of the luminous layer for explaining the quantum well structure of the light emitting diode of this invention

[Drawing 2]The sectional view showing the light emitting diode of the 1st example of this invention

[Drawing 3]The figure showing the band diagram of the light emitting diode

[Drawing 4]The figure showing EL spectrum of the light emitting diode

[Drawing 5]The figure showing the band diagram of the luminous layer for explaining the quantum well structure of the light emitting diode of other examples of this invention

[Drawing 6]The figure showing EL spectrum of the light emitting diode

[Drawing 7]The figure showing the band diagram of the light emitting diode of other examples of this invention

[Drawing 8]The figure showing the band diagram of the light emitting diode of a comparative example

[Drawing 9]The figure showing PL spectrum of the light emitting diode

[Drawing 10]The figure showing the light emitting diode of the double hetero structure of a conventional example

[Drawing 11]The mimetic diagram of the active layer of the light emitting diode

[Drawing 12]The figure showing EL spectrum of the light emitting diode

[Drawing 13]The figure showing PL spectrum of the light emitting diode

[Description of Notations]

1 n lateral electrode

2 Gallium arsenide (GaAs) board

3 N type ZnSSe cladding layer

4 ZnCdSe layer

5 The ZnSe layer of Te dope

6 P type ZnSSe cladding layer

7 P type inclination potential layer

8 p lateral electrode

11 ZnSe substrate

12 A n type ZnSe contact layer

13 The ZnSeTe active layer of i (genuineness) mold

14 A p type ZnSe contact layer

15 ZnSeTe layer

16 HgSe layer

17 and 18 Metal electrode

21 N type ZnMgSSe layer

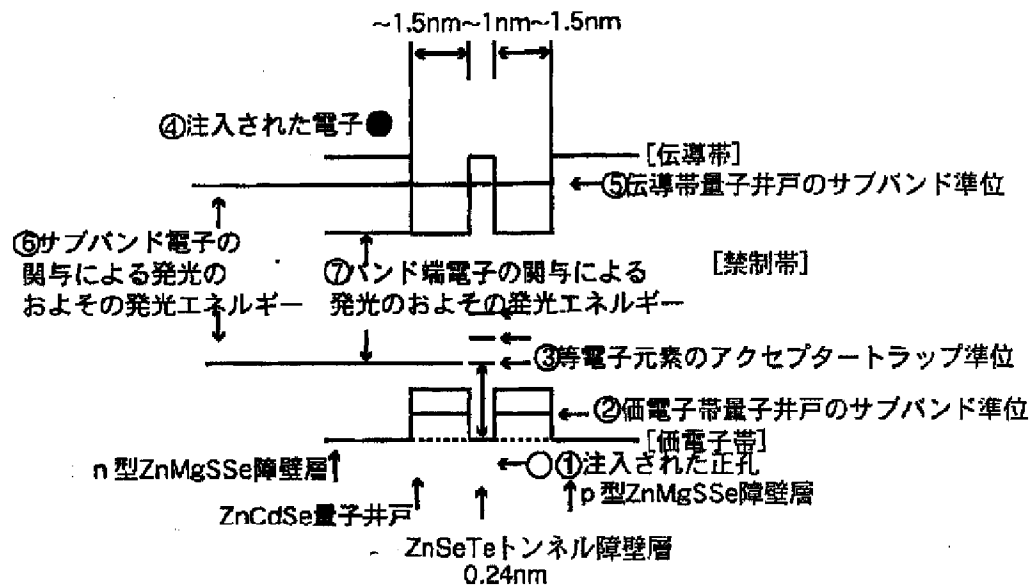
22 P type ZnMgSSe layer

23 Intrinsic (i type) ZnCdSe layer

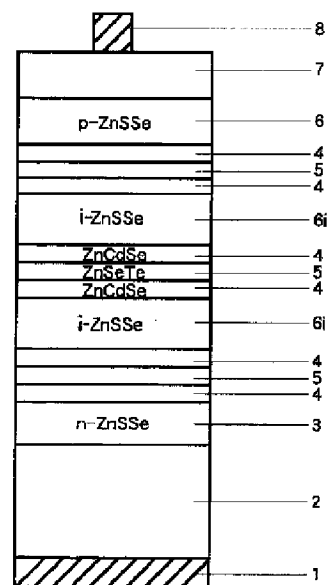
24 The ZnSe barrier insertion layer which added Te

## DRAWINGS

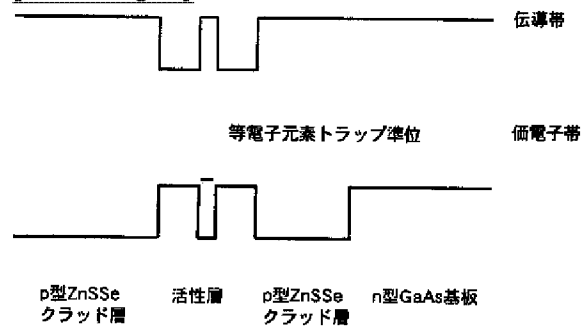
[Drawing 1]



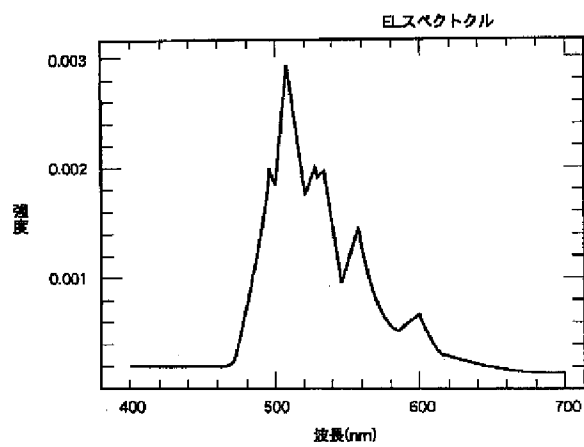
[Drawing 2]



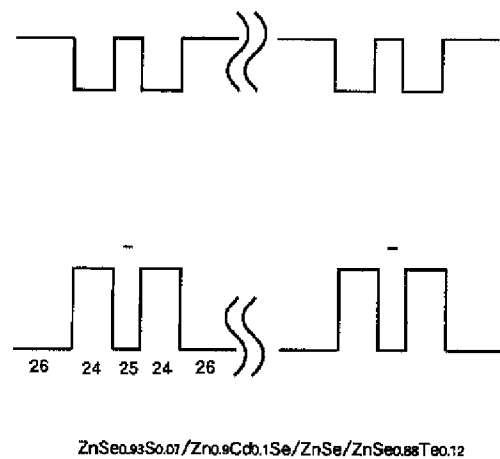
[Drawing 3]



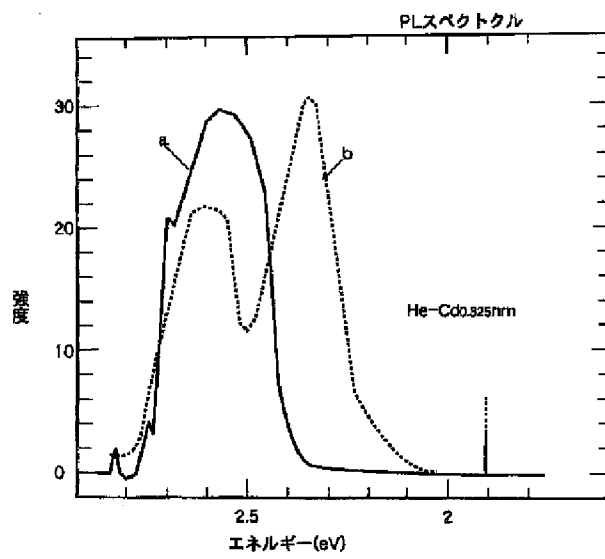
[Drawing 4]



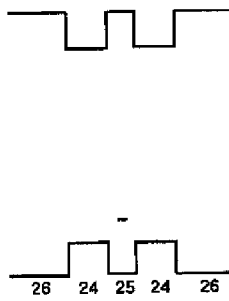
[Drawing 5]



[Drawing 6]

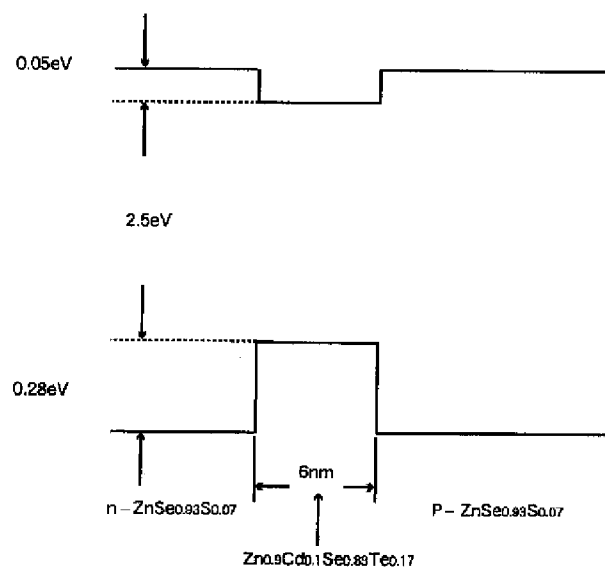


[Drawing 7]

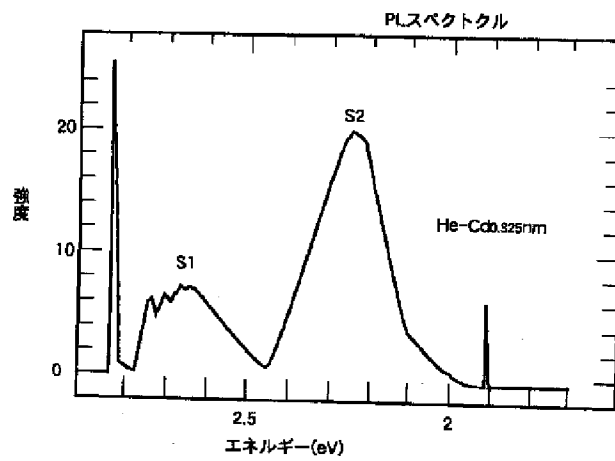


$\text{ZnSe}_{0.93}\text{S}_{0.07}/\text{Zn}_{0.88}\text{Cd}_{0.14}\text{Se}/\text{ZnSe}/\text{ZnSe}_{0.88}\text{Te}_{0.12}$

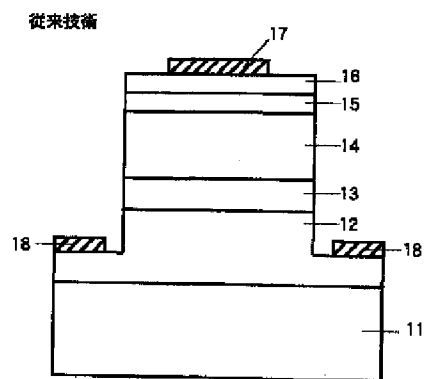
[Drawing 8]



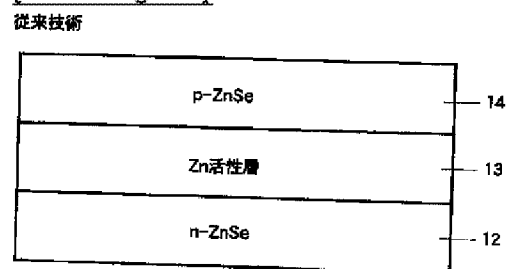
[Drawing 9]



[Drawing 10]

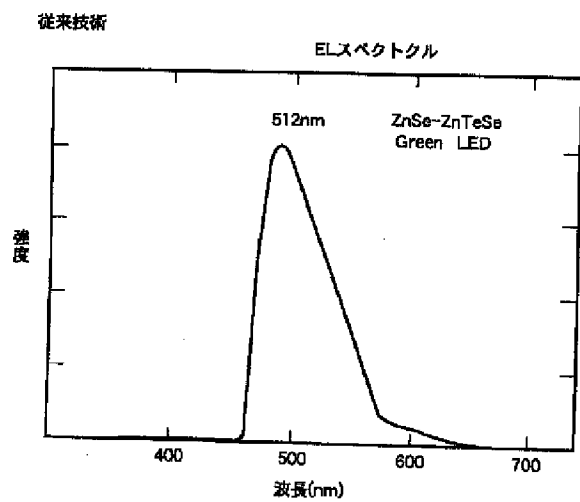


[Drawing 11]





[Drawing 12]



[Drawing 13]

